Reactive polymeric microspheres: Catalytic reduction of a nitrobenzene derivative

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ABSTRACT: Polymeric microspheres have been demonstrated as a potentially useful vehicle for targeted delivery applications. In this work we report on the preparation of polymer microspheres capable of performing specific reaction chemistry. The microspheres are modified with silver nanoparticles in a two-step reaction. The first step involves formation of the microsphere by UV-induced polymerization of pyrrole and the second step is the reduction of silver cations to metallic silver *in situ*. The resulting Ag-decorated microspheres were characterized by scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, energy dispersive X-ray, and thermogravimetry analysis. The catalytic reaction behavior of the decorated microspheres was illustrated through the reduction reaction of *m*-nitrobenzene sulfonate acid in the presence of sodium borohydride. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43653.

INTRODUCTION

Polymer microspheres are a class of materials that show substantial promise in applications such as targeted delivery, controlled release, and potentially for chemical sensing, depending on the contents of the microspheres and the permeability of the encapsulating polymer film.[1,2] While it is possible to form polymer microspheres from a number of monomer precursors, polypyrrole has proven to be a useful material for the construction of these structures. The reasons for the utility of polypyrrole in this application are its conductivity in its doped state, its ability to undergo polymerization by optical, electrochemical, or chemical means. While much of the work to date has centered on encapsulation, it is also possible that these microspheres can participate in reaction chemistry, depending on the system.

Metal nanoparticles (NPs) have attracted much attention because of their ability to function as heterogeneous catalysts, microelectronic devices, drug delivery carriers, and chemical sensors.[3–5] In all of these cases, the surface area to volume ratio of the metal needs to be maximized to achieve best efficiency. Gold, palladium, platinum, and silver nanoparticles have been used as catalysts in several reactions. Au NPs were used to catalyze both oxidation and reduction reactions in fuel cells.[6] Platinum NPs are used for catalytic applications including hydrogenation reactions and carbon–carbon bond formation.[7,8] Palladium NPs have been used as catalysts for coupling reactions of aryl halides.[9] Ag NPs reveal unique properties as an active catalyst for electrochemical reduction of CO_2 and the reduction of nitro containing compounds to amino functionalities.[10–13] It is the latter capability that we focus on in this work.

Hybrid materials, such as conducting polymers modified with metal nanoparticles can exhibit improved properties in comparison to polymers without metal modification.[14,15] Polypyrrole (PPy) is a widely used conductive polymer because of its environmental stability, it is nontoxic, easy to synthesize, and has facile redox properties.[16–18] In recent years a variety of functional materials based on PPy have been reported, including Ag-PPy wires,[19] Au-PPy capsules,[20] and Fe_2O_3-PPy nanotubes.[21] While chemical and electrochemical methods are well established for the preparation of PPy, photochemical polymerization is still rarely used. We have recently shown that photopolymarization can effectively be used to obtain hollow polypyrrole nano- and microvessels.[22,23] Template synthesis is the most intensely studied method to control size and shape of polymeric nano- and microstructures. Few studies have been reported on the use of soft-templating methods without the use of surfactants as a means to control nano- and microscale structure.

In this work, we examine the viability of an emulsifier-free emulsion polymerization to control PPy morphology, modify
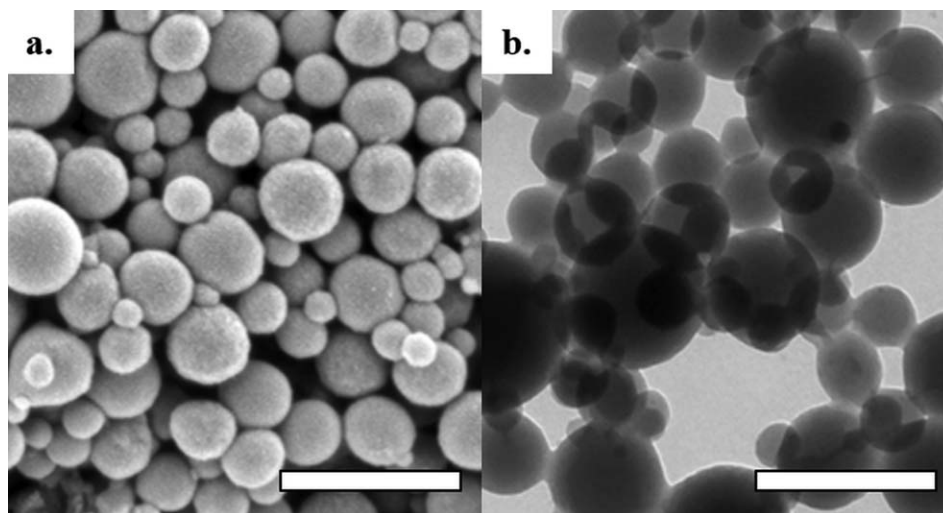
Figure 1. (a) SEM and (b) TEM images of the PPy microspheres as prepared by the emulsifier free emulsion photopolymerization of pyrrole/chloroform in water. Scale bar represents 500 nm.

polymeric structures with silver nanoparticles and test the product for its application as a catalyst in the reduction of nitroaromatics to aniline derivatives. We have shown previously that three-dimensional hollow structures of polypyrrole can be synthesized via water in chloroform emulsion. Here we report on the two-step synthesis of solid polypyrrole microspheres decorated with silver nanoparticles: synthesized by photopolymerization via the reverse emulsion of chloroform in water, first, without the use of any surfactant or hard template followed by the incorporation of Ag NPs into polymeric matrix and validating the use of the polypyrrole microspheres as a catalyst support.

EXPERIMENTAL

Preparation of Polypyrrole (PPy) Microspheres Modified with Silver Nanoparticles

All chemicals were of the highest quality available commercially and aqueous solutions were prepared with water from a Milli-Q Plus water purification system. An emulsion was prepared by the addition of 25 μL chloroform (POCH, 98.5%) and 50 μL pyrrole (Aldrich, 98%) to 5 mL water and sonicated for 30 s at 400 W. The emulsion was subsequently placed in a quartz container for photopolymerization. To photopolymerize pyrrole, the quartz container was irradiated with UV light from a mercury lamp (Polamp-5, Poland, 80 W) for 30 min at a distance of 10 cm from the reaction solution. The resulting PPy microspheres were separated from the supernatant liquid by centrifugation. Silver nanoparticles were formed by the addition of 100 μL of a 0.001 mol dm^{-3} AgNO$_3$ to the dry PPy vessels. After 4 h of conditioning in the AgNO$_3$ solution, the PPy vessels were again separated by centrifugation and washed with water. The centrifugation and washing steps were repeated three times.

The Ag-PPyNP structures were imaged using a LEO 1530 scanning electron microscope. The transmission spectra of polypyrrole microspheres and Ag-PPy microspheres were recorded in KBr pellets using Nicolet 6700 FTIR spectrometer.

Thermogravimetric measurements were performed under an oxygen atmosphere using a TGA Q50 (TA Instruments).

An Energy Dispersive X-ray detection system mounted on the LEO1530 FESEM microscope was used to perform elemental analysis of the samples. Additionally, a JEM 1400 transmission electron microscope was used to image the silver nanoparticle-modified and unmodified PPy vessels.

### Catalytic Measurements Using PPy Microspheres Modified with Silver Nanoparticles

A 200 μL suspension of the Ag-PPy microspheres (0.02 mg) and 100 μL (0.0002 mol dm^{-3}) of sodium 3-nitrobenzenesulfonate (m-NBS) (Aldrich, 98%) were added to 1.65 mL of water and sonicated for 20 minutes. A 50 μL aliquot of 0.1 mol dm^{-3} NaBH$_4$ solution was then added under vigorous stirring. The resulting suspension was placed in a quartz cuvette, and ultraviolet-visible spectra were recorded. Spectra were obtained on an Ocean Optics USB4000 UV-visible spectrophotometer from 200 to 700 nm.

RESULTS AND DISCUSSION

The primary purpose of this work is to demonstrate that PPy microspheres can readily incorporate nanoparticle catalysts and these composites can be used as a catalyst. In the discussion that follows we consider the issues associated with the formation of these composite materials and then the actual use of these materials as catalysts.

Formation of the Composite Materials

Synthesis of Polypyrrole Microspheres. Preparation of the PPy microspheres involves the formation of a chloroform in water emulsion, followed by photopolymerization of the particles dispersed in the continuous water phase. In our previous work we have shown that photochemical polymerization of pyrrole occurs under irradiation with UV light ($\lambda < 400$ nm) in halogenated solvents such as chloroform and bromoform.[23,24] The photopolymerization of pyrrole occurs in the water/chlorinated solvent emulsion by irradiation under a mercury vapor lamp. Polymer grows on the water droplet surface, forming hollow
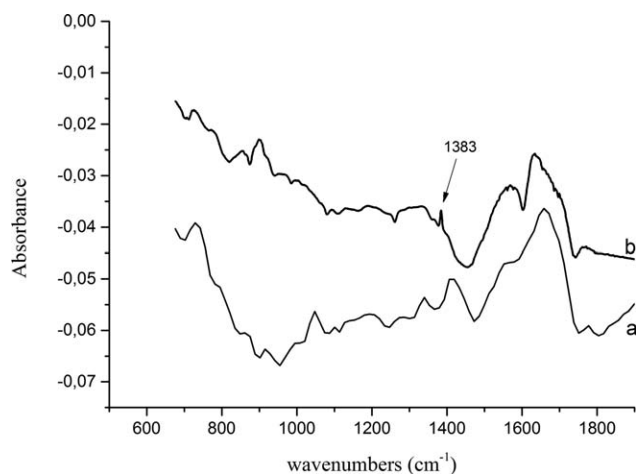
Figure 2. FTIR spectra of the PPy microspheres prepered by photopoly-merization: (a) nonmodified, (b) modified with silver nanoparticles.

polymeric particles, with an average size of about 700 nm.[23] In this work we use reverse emulsion of chloroform in water. This emulsion was placed in a quartz cuvette and exposed on UV light. This yields a dark precipitate, which can be separated through centrifugation. After separation, the deposit was imaged by scanning electron microscopy [SEM, Figure 1(a)]. It was found that the product consists of relatively uniform, spherical particles. The polypyrrole structures have diameters between 50 and 200 nm. Transmission electron microscopy (TEM) was used to evaluate whether or not the particles are hollow. Figure 1(b) shows the TEM image which indicates that using this procedure we can obtain solid microspheres rather than hollow

microcapsules. Polymeric sponge-like microspheres with large surface area can be useful as a catalyst support material.

Incorporation of Silver Nanoparticles into PPy Spheres. Poly-pyrrole obtained through photopolymerization in chloroform is in a poorly doped state and the counter ion Cl^- enters into the PPy matrix as dopant.[23] Polypyrrole could be transformed to a more highly doped state by an oxidant such as $AgNO_3$. Ag^+ ions are reduced to Ag^0 by polypyrrole, simultaneously converting the reduced PPy to a doped, oxidized form of PPy (Ag-PPy), and NO_3^- is also present as the dopant.[25]

FTIR spectroscopy was used to examine the structure of the pure PPy and Ag-PPy samples (Figure 2). The FTIR spectrum of pure PPy reveals several vibrational modes attributable to polypyrrole.[26] In the FTIR spectra, the bands centered at 1550 and 1410 cm^{-1} correspond to the C–C and C–N vibrations in pyrrole rings. The C–N or C–H in-plane deformation modes appear at 1333 and 1290 cm^{-1}. The peak at 969 ascribed to the C–C out-of-plane bending vibration, while other bands at 920 and 733 cm^{-1} are C–H out-of-plane deformation. The FTIR spectrum of Ag-PPy is similar to the pure PPy spectrum except band at 1383 cm^{-1}. This band is attributed to the N–O symmetric stretch which indicated that the Ag-PPy was doped by NO_3^-.[27]

The incorporation of silver nanoparticles into the PPy microspheres is a simple process involving the addition of a 0.001 mol dm^{-3} $AgNO_3$ solution to the PPy microspheres and conditioning in solution for 4 h. During the conditioning process the silver is reduced by the PPy and incorporated into the sponge-like nanostructure of the spheres. Reduction of Ag^+ ions takes place within the polypyrrole matrix and after the
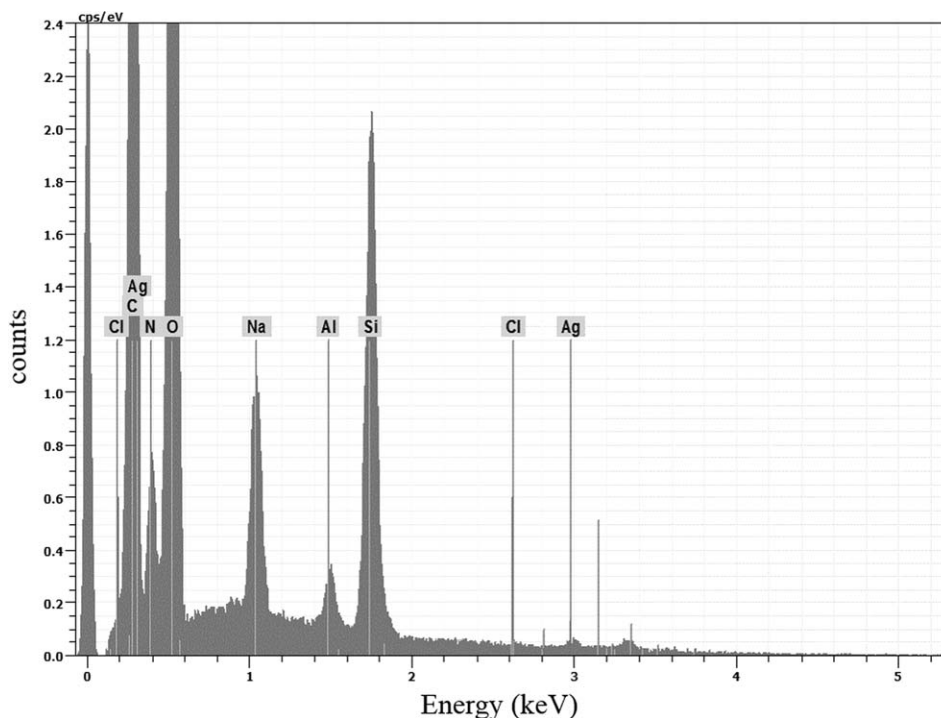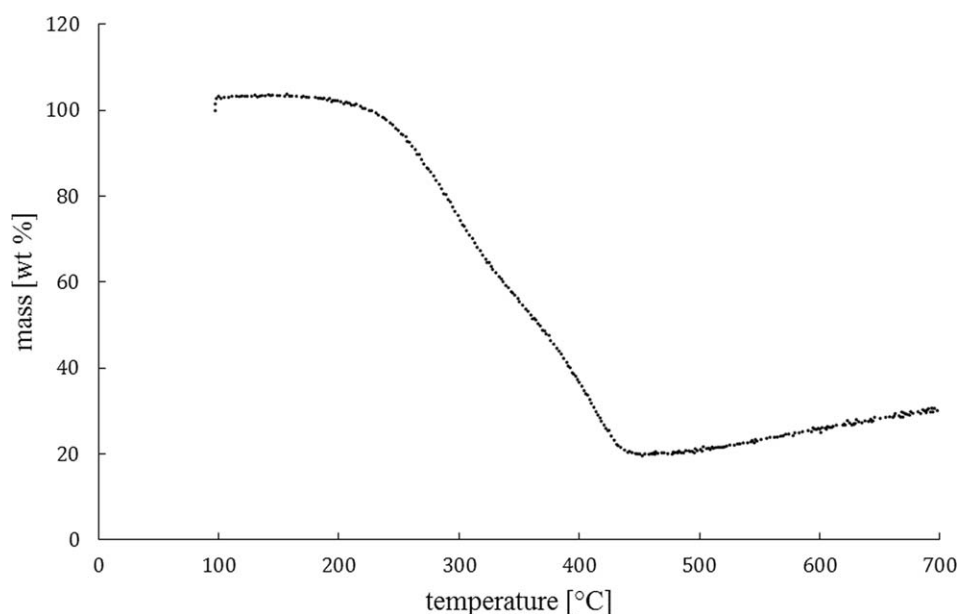

Figure 3. EDS spectrum of the PPy microspheres modified with silver nanoparticles.
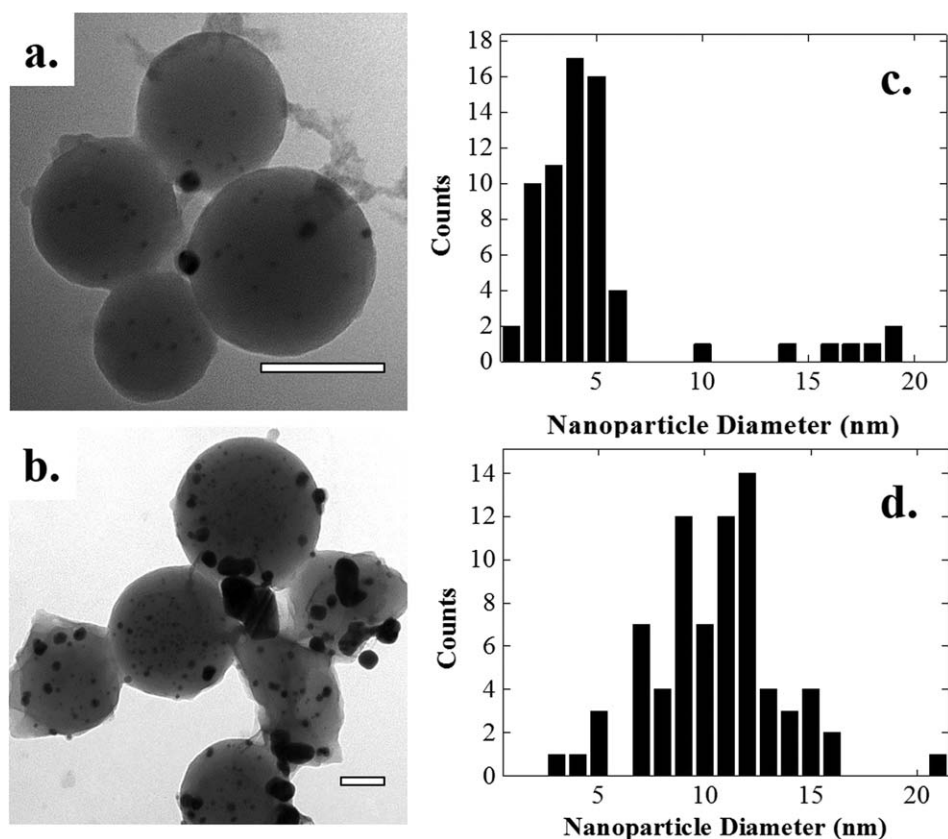
Figure 4. TEM images of the PPy microspheres modified with silver nanoparticles after conditioning in (a) 0.001 mol dm^{-3} and (b) 0.1 mol dm^{-3} AgNO$_3$. Scale bar represents 100 nm. Histograms showing the size and distribution of the silver nanoparticles prepared in (c) 0.001 mol dm^{-3} and (d) 0.1 mol dm^{-3} AgNO$_3$.

formation of Ag nuclei, Ag$^+$ ions are absorbed onto the surface of growing Ag nuclei because of an ionic adsorption effect. After incorporation of silver nanoparticles, and subsequent separation, the presence of silver was confirmed by EDX (Figure 3).

Direct control over nanoparticle size and distribution occurs by simply changing the silver nitrate concentration. Figure 4(a,b) shows the particle size distribution of silver nanoparticles formed from a 0.001 mol dm^{-3} solution yielding particles averaging 4 nm

Figure 5. Thermogram of the PPy microspheres modified with silver nanoparticles.
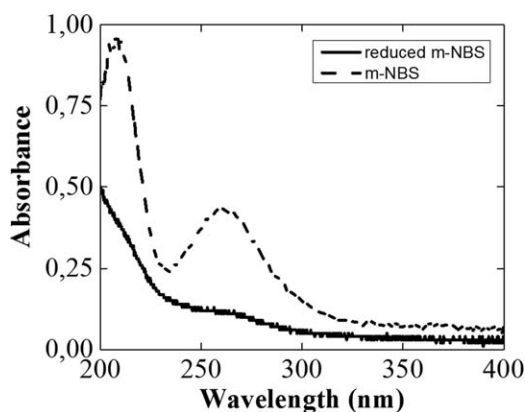
Figure 6. UV-Vis spectrum of m-NBS recorded before and after reduction with NaBH$_4$ in the presence of the PPy microspheres modified with silver nanoparticles.

in diameter and the corresponding TEM image. Diameter size range is relatively narrow, from 1 to 6 nm ($+/-$ 1.27 nm). Upon addition of a more concentrated 0.1 mol dm^{-3} silver nitrate solution, the average particle size becomes 12 nm, and the distribution becomes much broader, in the range of 5–16 nm ($+/-$ 3.03 nm) [Figure 4(c, d)]. Silver nanoparticles are incorporated on the polymeric surface and imbedded into polypyrrole as well likely because of sponge-like structures of microspheres.

To estimate the weight percentage of the incorporated nanoparticles, we used thermogravimetry. The microvessels decorated with Ag NP were heated to 700 °C under an oxygen atmosphere to decompose the polymer phase, leaving the nanoparticles intact, and to determine the mass loss. Thermograms of polymer microvessels with Ag NP are shown in Figure 5. The initial mass of sample was 0.031 mg. For Ag-PPy, the mass remains stable up to 200 °C, then gradually decreases, with up to a 80% of mass loss, which is attributed to polymer decomposition. The final mass loss was around 0.0248 mg. At approximately 480 °C the sample mass increases, most likely because of oxidation of the silver nanoparticles at higher temperatures.[28] The above data demonstrate that the nanoparticles constitute approximately 20% (w/w) of the microvessels modified with Ag NP.

Catalytic Activity. Catalytic hydrogenation is an important process for introducing amine groups onto pharmaceutical and agricultural target compounds in an industrial setting. Catalytic reduction of nitro compounds to amino compounds using metal nanoparticles such as Ni, Pd as a catalyst and NaBH$_4$ has been reported.[29] The silver nanoparticles also exhibit catalytic properties in the presence of nitro compounds and sodium borohydride.[13] The catalytic activity of the as-prepared Ag-PPy microspheres were examined using m-NBS as the nitro-aromatic probe molecule. The catalytic activity of the Ag-PPy microspheres was examined using UV-Vis spectroscopy (Figure 6). The m-NBS molecule showed a strong absorbance at 261 nm. After addition of the Ag-PPy composite, a decrease of this maximum occurred immediately because of reduction of m-NBS to m-ABS (m-aminobenzenesulfonate). We calculated conversion percent (α) of m-NBS using the following equation, where c_0 is an initial concentration and c is a final concentration.

$$\alpha = \frac{c_0 - c}{c_0} \times 100\% \qquad (1)$$

The estimated conversion percentage was found to be 71%. Zhang et al. has been reported similar catalytic reaction with lower conversion percentage ($\alpha = 51.8\%$).[12] The catalytic efficiency in the metal particle catalysis can be dependent on catalyst size.[30] Because of relatively narrow diameter size range of silver nanoparticles more efficient catalyst was obtained.

CONCLUSIONS

We have investigated the synthesis of a Ag-PPy functional material by two steps. The first step involves the UV-induced polymerization of pyrrole, while the second step is the chemical reduction of silver ions in the matrix of the polypyrrole. The size of silver nanoparticles can be controlled by concentration of AgNO$_3$. The PPy-Ag matrix provides a porous structure with large effective surface area whereby the Ag-PPy composites exhibit high catalytic properties during the reduction of nitro compounds.

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